

FORM PTO-1390
(REV 11-98)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

57.0272PCT

TRANSMITTAL LETTER TO THE UNITED STATE
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, use 35 CFR 1.5

09/646715

INTERNATIONAL APPLICATION NO
PCT/GB99/00737INTERNATIONAL FILING DATE
22 March 1999PRIORITY DATE CLAIMED
20 March 1998

TITLE OF INVENTION HYDROPHOBIAALLY MODIFIED POLYMERS FOR WATER CONTROL

APPLICANT(S) FOR DO/EO/US Timothy Gareth John JONES; Gary John TUSTIN

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C.371(b) and PCT Articles 22 and 39(1)
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(3)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:
EXPRESS MAIL EK802769739US

09/646715 PCT/PTO 20 SEP 2000

17. ☐ The following fees are submitted

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO \$970.00International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$840.00International preliminary examination fee (37 CFR 1.482) not paid to USPTO but
international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$760.00International preliminary examination fee paid to USPTO (37 CFR 1.482)
but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$670.00International preliminary examination fee paid to USPTO (37 CFR 1.482)
and all claims satisfied provisions of PCT Article 33(1)-(4) \$96.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

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NAME

34,476

REGISTRATION NUMBER

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Hydrophobically Modified Polymers for Water Control

The present invention relates to cross-linkable hydrophobically modified water-soluble polymers for reducing the water
5 production of a hydrocarbon well drilled through subterranean formations. More particularly it relates to such polymers and polymer containing compositions for selectively reducing the flow of subterranean aqueous fluids into a well while maintaining the hydrocarbon production.

10

BACKGROUND OF THE INVENTION

During the life cycle of a hydrocarbon well, e.g., a well for
15 extracting oil or natural gas from the Earth, the producing well commonly also yields water. In these instances, the amount of water produced from the well tends to increase over time with a concomitant reduction of hydrocarbon production. Frequently, the production of water becomes so profuse that remedial measures
20 have to be taken to decrease the water/hydrocarbon production ratio. As a final consequence of the increasing water production, the well has to be abandoned.

Various techniques have been developed and used for reducing the
25 quantity of water produced from oil and/or gas wells. For example, US Pat. No. 3,719,228 discloses a method of treating a subterranean formation containing hydrocarbons and brine to stimulate the production of hydrocarbons: A preflush composition comprised of a water solution of rosin soap and fatty acid soap
30 is injected into the formation. The preflush reacts with connate brine to produce a precipitate that blocks the brine-bearing passages. The composition does not react with hydrocarbons thereby allowing hydrocarbon-bearing passages to remain open. Another alternative method is disclosed in US Pat. No.
35 4,617,132: A sandstone formation is contacted with an aqueous solution containing a water soluble anionic polymer having a molecular weight greater than 100,000. As the next step, the

- 2 -

anionic polymer is contacted with a fluid containing a water soluble cationic polymer having a weight greater than 1,000. As a result of the contact of the anionic with the cationic polymer, coacervation occurs between the two polymers which reduces the amount of the anionic polymer removed from the formation by fluids produced therefrom. The presence of stabilized polymer in the formation reduces the water/oil ratio by reducing the permeability of the formation to water in the wellbore area.

In yet another technique, disclosed in US Pat. No. 5,203,834, comprises the steps of injecting a gas, a polymer composition capable to form a foamed gel with the gas, and a delayed gel degrading agent being capable of opening pathways in the gel.

The gelation of high molecular weight polymers ($M_w > 10^6$ g/mol) has been extensively used in the development of water-based treatment fluids for water control is further described for example by R. D. Sydansk in "Acrylamide-polymer/chromium(III)-carboxylate gels for near wellbore matrix treatments", 7th SPE Symp. Enhanced Oil Recovery, Tulsa, Ok., April 1988, SPE/DoE 20214, or by R. S. Seright in: "Placement of gels to modify injection profiles", SPE/DoE Symp. Enhanced Oil Recovery, Tulsa, Ok., April 1994, SPE 27740. Typically for those methods, an aqueous solution of a high molecular weight polymer, such as a polyacrylamide/polyacrylate copolymer (a so-called partially-hydrolysed polyacrylamide), is gelled in situ in a porous formation using a metal cross-linker such as Cr^{3+} or small water-soluble organic cross-linkers such as formaldehyde and formaldehyde/phenol. Other water-soluble polymers such as poly(vinyl alcohol), the polysaccharide guar gum and the copolymer poly(vinylpyrrolidone-co-2-acrylamido-2-methyl-1-propanesulphonic acid) which can be cross-linked with a variety of cross-linking agents such as Zr^{4+} and boric acid.

A more recent approach is described by A. Keller and K. A. Narh in: "The effect of counterions on the chain conformation of polyelectrolytes, as assessed by extensibility in elongational

- 3 -

flow: the influence of multiple valency", J. Polym. Sci.: Part B: Polymer Phys., 32, 1697-1706 (1994). It includes the cross-linking of poly(sodium 4-styrenesulphonate) using Al^{3+} ions to form a gel. The concentration of the high molecular weight hydrophilic polymers used to form hydrogels is typically in the range 3-10 g/l.

Hydrophobically-modified polymers as such and their application as thickening agents in aqueous fluids has been extensively described. The principal application of these polymers is as viscosifying agents and they are commonly referred to as associative thickeners; these polymers are also known as polysoaps. The associative behaviour is generated by a small mole fraction (typically ≤ 0.05) of hydrophobic groups which, as separate monomers, are not soluble in water. The hydrophobic groups undergo intermolecular association in aqueous solution above the overlap concentration which results in a significant increase in solution viscosity.

Hydrophobically-modified polymers can be gelled in the presence of monomeric surfactants. For example, large increases in the viscosity of solutions of hydrophobically-modified poly(acrylic acid) in the presence of anionic, cationic and non-ionic surfactants have been disclosed. A brief review of the interaction between hydrophobically-modified polymers and surfactants can be found in: Lindman, B. and Thalberg, K., "Polymer-surfactant interactions - recent developments" in Interactions of Surfactants with Polymers and Proteins, E.D. Goddard and K.P. Ananthapadmanabhan (eds.), pp. 203-276, CRC Press, Boca Raton, Florida (1992).

In the U.S. Patent No. 4,532,052, the use of branched organic polymers for various well treating operations is described. The known polymers include hydrophilic and combinations of hydrophilic and hydrophobic side groups. The preferred examples are characterized as having large hydrophilic branches.

- 4 -

In the U.S. Patent No. 5,003,006, there are described cross-linked block copolymers containing polar and non-polar segments, with the polar segments generally making up at least 50 per cent.

It is the object of the invention to provide new polymers for water control application.

SUMMARY OF THE INVENTION

According to a first aspect of the invention, hydrophobically modified water-soluble polymers are provided which are capable of being chemically cross-linked to produce permanent gels in water-bearing formations. The polymers are characterized by a linear chain or backbone and attached thereto hydrophobic side groups at random locations. The term "linear" is defined as the absence of extended side groups/chains others than the hydrophobic groups. The term "extended" can be interpreted as having a molecular weight of more than 200.

It has been found that hydrophobically modified polymers when based on block copolymers, tend to form an inferior gel presumably due to presence of inhomogeneous gelation. In addition there is economic advantage when producing polymers with high molecular weight through a random co-polymerization process. The use of large polymers is advantageous as it reduces the polymer concentration required to achieve a desired level of viscosity. Within the scope of the present invention, a high molecular weight can be defined as a molecular weight in excess of 50,000, more preferably in excess of 100,000. A preferable upper limit for the size of the polymers is given by a molecular weight of 15 million, preferably 5 million, more preferably 500,000 or less.

The polymers preferably comprise low concentrations (0.5-5 mole percent) of hydrophobic monomers which randomly co-polymerise with the hydrophilic monomers to form random copolymers. The

- 5 -

- hydrophilic units of the polymer, which constitute preferably 95-99.5 mole percent of the polymer chain, contain preferably at least some small fraction of functional groups which can be chemically cross-linked to produce a gel. Alternatively, the
- 5 hydrophobic groups themselves can contain chemical functions which can be the sites of cross-linking. Preferred hydrophobic groups are alkyl groups of more than six , preferably eight, and even more preferably 12 carbon atoms, and derivatives thereof.
- 10 Chemical cross-linking is defined as forming a chemical bond between the cross-linked polymers. Chemical cross-linking is understood to be stable and thermally irreversible. Some of the advantages in the use of hydrophobically modified polymers are responsiveness to hydrocarbons resulting in a reduction in the
- 15 adhesive strength of gels and an extreme retardation of gelation, and solubilisation of large organic cross-linking agents.

- The cross-linking agents can be either inorganic ions (or ionic
- 20 complexes) or polar organic molecules. When the polymer contains ionic groups such as carboxylate or sulphonate functions the polymer chains can be cross-linked by inorganic ions such as chromium(III) or zirconium(IV), frequently in the presence of ligands, such as acetate or adipate ions, to control the rate of
- 25 cross-linking. Alternatively, organic cross-linking agents can be used. For example, the amide groups on poly(acrylamide) can be cross-linked with formaldehyde or a mixture of formaldehyde and phenol. The disadvantages of using formaldehyde or similar small molecules are their toxicity and issues of disposal. The
- 30 larger reagents such as hexanal and heptanal, which are not classed as toxic, would be suitable cross-linking agents but are not sufficiently soluble in water to cross-link normal hydrophilic polymers such as the poly(acrylamide)/poly(acrylate) copolymer. However, these larger cross-linking agents are
- 35 solubilised in aqueous solutions by hydrophobically-modified poly(acrylamide) polymers and can thence cross-link them.

These and other features of the invention, preferred embodiments and variants thereof, and further advantages of the invention will become appreciated and understood by those skilled in the art from the detailed description following below.

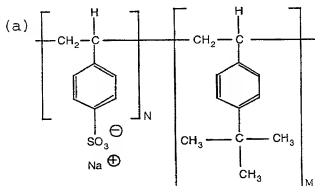
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MODE(S) FOR CARRYING OUT THE INVENTION

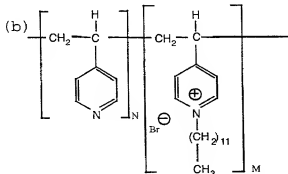
A large number of hydrophobically-modified polymers are known as such and suitable for the purpose of the present invention.

These polymers are based on the modification of common water-soluble (hydrophilic) polymers such as poly(acrylamide), poly(acrylic acid), poly(vinylpyridine), hydroxyethylcellulose and poly(ethylene oxide). The structure of examples of

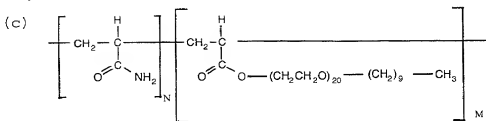
hydrophobically-modified polymers are given below for poly(sodium 4-styrenesulphonate) (a), poly(vinylpyridine) (b), and poly(acrylamide) (c):



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- 7 -

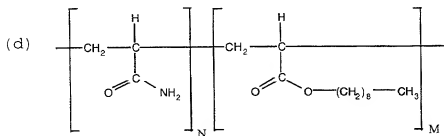


The fraction $M/(M+N)$ denotes the mole fraction of hydrophobic monomers in the polymer.

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The following formulae describe the structure of further examples which can be readily cross-linked using known cross-linkers.

- 10 The structure of a hydrophobically-modified poly(acrylamide) where the hydrophobic modification takes the form of replacing about 3 mole percent ($M/(M+N)=0.03$) of the acrylamide units with the hydrophobic monomer n-nonyl acrylate is:

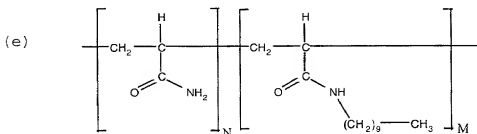


15

This polymer has an average molecular weight of about 5×10^6 g/mole and it can be readily cross-linked with chromium(III) or zirconium(IV) or the organic cross-linker hexanal. Where the gels formed by conventional poly(acrylamide)/poly(acrylate) copolymers undergo syneresis and shrink, the gels formed by hydrophobically-modified polymers in otherwise identical formulations undergo syneresis at approximately half the rate of the hydrophilic polymers. It is also observed that the cross-linking of the hydrophobically-modified poly(acrylamide) is less sensitive to the concentration of divalent ions (Ca^{2+} , Mg^{2+}).

The structure of another hydrophobically-modified poly(acrylamide) where the hydrophobic modification takes the

form of replacing about 1 mole percent ($M/(M+N)=0.01$) of the acrylamide units with the hydrophobic monomer N-decylacrylamide is:



5

This polymer can also be cross-linked using metal ions (Cr(III), Zr(IV)) and organic molecules (hexanal).

- 10 An additional feature of hydrophobically-modified polymers such as (d) and (e) is that they can be prevented from cross-linking in contact with hydrocarbon. The prevention of cross-linking can arise from two possible mechanisms. Firstly, the larger organic cross-linker can be removed from the polymer solution by
- 15 solubilisation in the contacting hydrocarbon. The cross-linker hexanal, which is solubilized by the hydrophobically-modified polyacrylamide, is readily soluble in hydrocarbon and can be extracted from the polymer solution. Secondly, the solution of hydrophobically-modified polymer can partly solubilize the
- 20 hydrocarbon which itself can be sufficient to prevent cross-linking. Thus a solution of hydrophobically-modified poly(acrylamide) with the metal ion cross-linker such as Cr(III) or a small water-soluble cross-linker such as formaldehyde can be prevented from cross-linking when mixed with hydrocarbon.

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- 10 -

CLAIMS

1. A composition for selectively blocking water bearing
subterranean formations, said composition comprising water
soluble polymers having a linear hydrophilic backbone with
hydrophobic side groups located at random positions along
said backbone and functional groups for cross-linking said
polymers, said composition forming a cross-linked gel in a
subterranean water-bearing formation.
2. The composition of claim 1, wherein the polymers comprise 0.5
to 5 mole per cent of hydrophobic side groups.
3. The composition of claim 1, wherein the functional groups for
cross-linking form part of the hydrophilic backbone of the
polymer.
4. The composition of claim 1, wherein the functional groups for
cross-linking form part of the hydrophobic side groups.
5. The composition of claim 1, wherein the polymers have a
molecular weight of 50,000 or more.
6. The composition of claim 1, further comprising a chemical
cross-linking agent.
7. The composition of claim 6, wherein the chemical cross-
linking agent is organic.
8. The composition of claim 6, wherein the chemical cross-
linking agent is an aldehyde or aldehyde derivative
comprising at least 5 carbon atoms.
9. The composition of claim 8, wherein the chemical cross-
linking agent is hexanal or heptanal.

Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

DECLARATION FOR PATENT APPLICATION☐ Declaration Submitted **WITH** Initial Filing **OR** ☒ Declaration Submitted **After** Initial Filing**Attorney Docket Number:****First-Named Inventor:**

57.0272

Timothy Gareth John Jones

COMPLETE IF KNOWN:**Application Number:**

09/646,715

Filing Date:

September 20, 2000

Group Art Unit:**Examiner's Name:**

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

HYDROPHOBICALLY MODIFIED POLYMERS FOR WATER CONTROL

the specification of which:

☐ is attached hereto as Attorney Docket No.: _____**OR**☒ was filed on September 20, 2000 _____ ☒ as United States Application No. 09/646,715 or☐ PCT International Application No. _____☐ and was amended on _____ (MMDDYY).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 1.19(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application Numbers	Country	Foreign Filing Date (MMDDYY)	Priority Not Claimed	Certified Copy Attached? Yes	No
9805880.3	GB	20-MAR-98		<input type="checkbox"/>	<input checked="" type="checkbox"/>
PCT/GB99/00737	WO	22-MAR-99		<input type="checkbox"/>	<input checked="" type="checkbox"/>

☐ Additional foreign application numbers are listed in a supplemental priority data sheet PTO/SB/02B, attached hereto.

Please type a + sign inside this box ☐

Based on PTO/SB/01 (3/97)
Approved for use through 9/30/98. OMB 0651-0032
Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE

☐ I hereby claim the benefit under Title 35 U.S.C. § 1.19(e) of any United States provisional application(s) listed below.

Application Number	Filing Date

☐ Additional provisional patent application numbers are listed in a supplemental priority data sheet PTO/SB/02B, attached hereto.

I hereby claim the benefit under 35 U.S.C. § 1.20 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph 35 of U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

US Parent Application Number	PCT Parent Number	Parent Filing Date (MMDDYY)	Parent Patent Number (if applicable)
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☐ Additional US or PCT international application numbers are listed in a supplemental priority data sheet PTO/SB/02B, attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agents(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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Steve Christian	<u>38,106</u>	Peter Y. Lee	<u>30,865</u>
Brigitte Jeffery	<u>38,925</u>	William L. Wang	<u>39,871</u>
Douglas Y'Barbo	<u>42,739</u>		
Jaime Castano	<u>41,660</u>		

☐ Additional registered practitioner(s) named on supplemental Registered Practitioner Information Sheet PTO/SB/02B, attached hereto.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the

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United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00
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G. J.
(Initial)

Jones
(Last)

Inventor's Signature:



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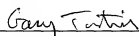
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